

Hydrogen peroxide, methyl hydroperoxide, and formaldehyde over North America and the North Atlantic

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[1] Hydrogen peroxide (H_2O_2), methyl hydroperoxide (CH_3OOH), and formaldehyde (CH_2O) were measured over North America and the North Atlantic during the INTEX-NA, TOPSE, and SONEX aircraft campaigns. An overview of H_2O_2 , CH_3OOH , and CH_2O across the geographic and temporal range of these campaigns is presented. H_2O_2 , CH_3OOH , and CH_2O mixing ratios and variability were larger during INTEX-NA compared to TOPSE and SONEX. Mean H_2O_2 , CH_3OOH , and CH_2O were 1390, 440, and 480 pptv, respectively, more than two times higher than TOPSE measurements and an order of magnitude higher than SONEX measurements. This is attributed to higher solar radiation levels and the more polluted conditions of INTEX-NA. Mixing ratios and variability decreased with altitude for all three gases and on all three campaigns, except for CH_3OOH during TOPSE. The impact of convection on H_2O_2 , CH_3OOH , and CH_2O is also discussed. Using the ratio $\text{H}_2\text{O}_2/\text{CH}_3\text{OOH}$, convectively influenced air parcels were found to be enhanced in CH_3OOH , CH_2O , CO, NO, and NO_2 while H_2O_2 and HNO_3 were depleted by wet removal. Biomass burning was also shown to increase H_2O_2 , CH_3OOH , and CH_2O mixing ratios up to 1.5, 2, and 1 ppbv, respectively, even after 4–5 days of transit. Results from this study show considerable variability in H_2O_2 , CH_3OOH , and CH_2O throughout the North American and North Atlantic troposphere. The variability in the upper troposphere is driven by local photochemical production and transport via regional convection and long-range pathways, suggesting transport mechanisms are important factors to include in photochemical models simulating H_2O_2 , CH_3OOH , CH_2O , and HO_x .

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1. Introduction

[2] The NASA Intercontinental Transport Experiment—North America (INTEX-NA) mission investigated the outflow of pollution from North America to the North Atlantic with a focus on understanding the transport and evolution of ozone (O_3) and O_3 precursors. INTEX-NA, the first phase of the NASA INTEX campaign, was conducted from June to August 2004 with twenty flights extending from California to the mid North Atlantic (Figure 1) [Singh *et al.*, 2006]. A full suite of chemical species was investigated during this mission including HO_x

precursors, hydrogen peroxide (H_2O_2), methyl hydroperoxide (CH_3OOH), and formaldehyde (CH_2O). A critical analysis of the distribution of hydroxyl radical precursors, along with the hydroxyl radical (HO), the perhydroxyl radical (HO_2), nitrogen oxides (NO_x), and hydrocarbons (HCs), is necessary to understand O_3 production over North America and the North Atlantic during the summer.

[3] H_2O_2 , CH_3OOH , and CH_2O contribute about 30% of the gross odd-hydrogen production in the troposphere with the remainder of production coming from the photolysis of ozone in the presence of water vapor [Lee *et al.*, 1997]. In regions where water vapor is limited, such as in the upper troposphere (UT), H_2O_2 , CH_3OOH , and CH_2O become more important HO_x reservoirs [Finlayson-Pitts and Pitts, 1986; Jaeglé *et al.*, 2000, 1999; Tan *et al.*, 2000]. CH_3OOH has the potential to produce one HO and up to three HO_2 molecules when photolyzed and the subsequent photolysis of CH_2O is considered [Logan *et al.*, 1981]. Hydrogen peroxide has a much smaller impact on UT HO_x levels because of its high solubility and resulting removal by precipitation and in-cloud reactions with SO_2 [O'Sullivan *et al.*, 1999; Crawford *et al.*, 2000]. However, low SO_2

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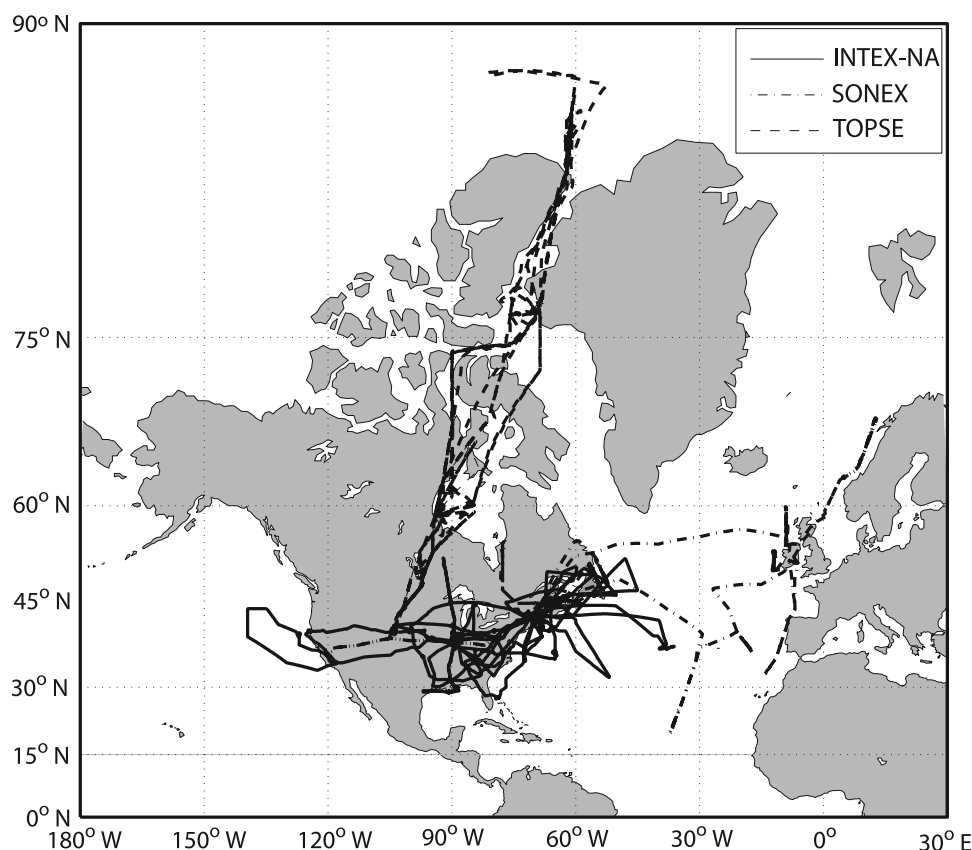


Figure 1. Flight tracks of INTEX-NA (over North America during the summer 2004), TOPSE (north and south transects over North America and Canada during the winter-spring 2000), and SONEX (over the North Atlantic during the fall 1997).

mixing ratios during INTEX-NA, indicate in-cloud reactions with SO₂ were not significant. As HO_x sinks, their sequestration in H₂O₂ and CH₃OOH followed by the loss of these compounds, results in the removal of three HO₂ radicals and an organic peroxy radical. This loss is a limit to net ozone production.

[4] Typically H₂O₂, CH₃OOH, and CH₂O have lower mixing ratios at higher altitudes. Therefore determining how these gases become elevated in the UT is of great interest. One possible source of H₂O₂ and CH₃OOH to the UT is convective vertical transport [Prather and Jacob, 1997]. For example, strong convective uplift in thunderstorms, typhoons [Newell et al., 1996], and widespread convective activity in regions such as the South Pacific Convergence Zone (SPCZ) and Inter Tropical Convergence Zone (ITCZ) [Pickering et al., 1992; Cohan et al., 1999; Gregory et al., 1999] may be important mechanisms for transporting HO_x precursors to the UT. UT enhancements of CH₃OOH in tropical and subtropical regions have been previously observed [Heikes et al., 1996a; Lee et al., 1995; Pickering et al., 1995; Newell et al., 1996; O'Sullivan et al., 1999] and these authors suggest convectively lifted boundary layer (BL) air, elevated in CH₃OOH, was the source of the observed enhancements. Although UT measurements of peroxides and CH₂O are limited over continents, elevated CH₃OOH associated with tropical air [Snow et al., 2003] and elevated CH₂O associated with long-range transport of its precursors [Fried et al., 2003a; A. Fried et al., The role

of convection in redistributing formaldehyde to the upper troposphere over North America and the North Atlantic during the summer 2004 INTEX campaign, unpublished manuscript, 2007, hereinafter referred to as Fried et al., unpublished manuscript, 2007] have been observed over North America.

[5] Care must be exercised in the interpretation of elevated CH₂O at high altitudes. The lifetime of CH₂O with respect to photolysis and OH is at most a few hours under sunlit conditions. Elevated CH₂O near clouds may be from convective injection, but a more likely scenario is CH₂O is elevated because of the injection of reactive hydrocarbons therefore serving as a tracer of lofted boundary layer reactive hydrocarbons (J. Crawford, personal communication, 2006; Fried et al., unpublished manuscript, 2007).

[6] Tropospheric photochemistry point models have been unable to exactly capture the vertical structure of HO_x, particularly in the UT where models both underestimate and overestimate HO_x levels [Jaeglé et al., 1997; Wang and Prinn, 2000; X. Ren et al., HO_x observations and model comparison during INTEX-NA 2004, submitted to *Journal of Geophysical Research*, 2006, hereinafter referred to as Ren et al., submitted manuscript, 2006]. Model studies have shown that peroxides impact HO_x levels when they are introduced into the UT through transport [Lee et al., 1995; Jaeglé et al., 1997; Prather and Jacob, 1997; Folkins et al., 1998; Cohan et al., 1999; Crawford et al., 2000]. The results in Crawford et al. [2000] showed elevated CH₃OOH

increased HO mixing ratios by 30–60% over a 50-hour period. Jaeglé *et al.* [1997] predicted that the injection of CH₃OOH would cause large increases in UT HO_x concentrations for more than a week downwind of the convective event. However, more recently, during INTEX-NA, point models under predicted HO₂ and HO by a factor of 3 above 8 km pointing to an unknown source of HO_x (Ren *et al.*, submitted manuscript, 2006). Studies have also shown CH₂O to be an important UT HO_x source [McKeen *et al.*, 1997]. In convective outflow over biomass burning regions, CH₂O is a significant source of HO_x and may stimulate UT O₃ production [Lee *et al.*, 1998]. Conclusions from model results indicate the injection of peroxides and CH₂O to the UT may be a source of not only local UT HO_x, but may also impact global HO_x distributions [Jaeglé *et al.*, 1997].

[7] It is important to note that these model studies [Lee *et al.*, 1995; Jaeglé *et al.*, 1997; Prather and Jacob, 1997; Folkins *et al.*, 1998; Cohan *et al.*, 1999; Crawford *et al.*, 2000] take place over tropical regions where peroxides and CH₂O are highly elevated in the BL and water vapor levels are relatively high. Over North America, HO_x production is primarily dominated by reactions of O(¹D) and H₂O at low latitudes and by CH₂O at high latitudes [Weinstein-Lloyd *et al.*, 1998; Cantrell *et al.*, 2003; Snow *et al.*, 2003]; H₂O₂ and CH₃OOH were shown to make only small contributions to the total UT HO_x budget. However, previously recorded measurements of peroxides spanning the troposphere over North America are limited, making INTEX-NA an important addition to peroxide distributions in this region, particularly during the summer months when photochemical production of peroxides is at a maximum.

[8] In this study we utilize in situ measurements from the INTEX-NA campaign and meteorological analyses to examine the hypothesis that convective transport is a source of HO_x precursors, H₂O₂, CH₃OOH, and CH₂O to the UT over North America and the North Atlantic. A companion paper by Fried and colleagues (Fried *et al.*, unpublished manuscript, 2007) further examines the role of CH₂O in this regard. In addition, this study compares the results of the INTEX-NA campaign to two earlier aircraft campaigns, Tropospheric Ozone Production about the Spring Equinox (TOPSE) [Atlas *et al.*, 2003; Cantrell *et al.*, 2003; Snow *et al.*, 2003] and Subsonic Assessment of Ozone and Nitrogen (SONEX) [Singh *et al.*, 1999; Thompson *et al.*, 2000], conducted over North America and the North Atlantic during different seasons (Figure 1).

2. Methods

2.1. H₂O₂ and CH₃OOH

[9] Measurements of H₂O₂ and CH₃OOH were made using a technique described by Lee *et al.* [1995]. Ambient air was sampled through an inlet on the side of the NASA-DC-8 and mixed with a collection solution in a continuous flow scrubbing coil. This technique scrubs peroxides from the ambient air into a collection solution (pH 6) based on the Henry's Law equilibrium partitioning. The aqueous solution was then analyzed using high-performance liquid chromatography with C-18 columns. The separated peroxides were then reacted with peroxidase and p-hydroxyphenyl-acetic acid to produce a fluorescent hydroperoxide derivative that was quantified using fluorescence detection. The gas phase

limits of detection (LOD) for H₂O₂ and CH₃OOH were 25 pptv and 20 pptv (2 sigma), respectively and the uncertainties were LOD \pm 30% of the ambient mixing ratio for 2 minute averaged samples. This technique has successfully been employed aboard the NASA DC-8, the NASA P3-B, and the NCAR C-130 research aircraft during previous airborne experiments [Heikes, 1992; Heikes *et al.*, 1996a, 1996b; O'Sullivan *et al.*, 1999, 2004; Snow *et al.*, 2003]. H₂O₂ was also measured using a new CIMS technique [Crounse *et al.*, 2006].

2.2. CH₂O

[10] CH₂O was measured using two separate techniques; the University of Rhode Island and United States Naval Academy (URI-USNA) group used a fluorometric method and the National Center for Atmospheric Research (NCAR) group used a tunable diode laser absorption spectroscopic (TDLAS) instrument (Fried *et al.*, unpublished manuscript, 2007). A comparison of results from these two techniques is found in section 2.2.3.

2.2.1. CH₂O (URI-USNA)

[11] CH₂O was measured with an automated fluorometric method adapted from Lazrus *et al.* [1988]. Gas phase CH₂O is removed from the atmosphere by mixing ambient samples with a pH 2 collection solution in glass stripping coils. The CH₂O reacts with H₂O to form the adduct dihydroxymethane (CH₂(OH)₂) which in the presence of the catalyst formaldehyde dehydrogenase (FDH) reacts with nicotinamide adenine dinucleotide (NAD⁺) to produce NADH. The fluorescence of NADH is proportional to the mixing ratio of CH₂O in the ambient sample. Prior to the mission, gas phase standards were added at the inlet under different pressures to calibrate the in-flight collection efficiency. Liquid standards were analyzed before each flight to calibrate the instrument. The CH₂O 2 sigma LOD was 50 pptv with an estimated uncertainty of 50 pptv \pm 30% of the ambient value for 1 minute averaged samples. The technique has been employed on previous aircraft and ground based experiments [Heikes, 1992; Lee *et al.*, 1998; O'Sullivan *et al.*, 2004].

2.2.2. CH₂O (NCAR)

[12] CH₂O was measured by the NCAR group using a tunable diode laser absorption spectroscopic (TDLAS) instrument. A detailed description of this instrument is found in Fried *et al.* [2003a, 2003b] and Wert *et al.* [2003]; therefore only a brief explanation will be given here. Sample air was pulled in through a heated PFA Teflon inlet (\sim 35°C and 1.3 cm OD) at \sim 9 standard liters per minute. The air then passed through a multipass Herriott cell where it absorbed the infrared (IR) radiation (3.5 μ m, 2831.6 cm⁻¹) from a tunable diode laser passing back and forth through the cell (total path length of 100 m). An IR detector was used to measure the amount of IR absorption by the ambient CH₂O. This technique, with minor modifications, has been previously used to measure CH₂O on a number of aircraft campaigns [e.g., Fried *et al.*, 2003a, 2003b; Wert *et al.*, 2003]. Averaged over the entire campaign, the 2 sigma LOD for 1-min measurements was 78 pptv. Starting with flight 14 on 31 July 2004 improvements in the mechanical stability of various optical components improved the LOD to 66 pptv. The systematic uncertainty at the 2 sigma level was estimated at 12% of

Table 1. Mean/Median and (Range) of H₂O₂, CH₃OOH, and CH₂O Mixing Ratios for Each Mission^a

	INTEX-NA	TOPSE	SONEX
H ₂ O ₂	1390/1070 (LOD-13180)	170/150 (LOD-1330)	120/80 (LOD-670)
CH ₃ OOH	440/350 (LOD-2150)	180/150 (LOD-1400)	50/30 (LOD-340)
CH ₂ O-URI-USNA	480/210 (LOD-4220)		70/30 (LOD-460)
CH ₂ O-NCAR	790/360 (LOD-6780)	120/90 (LOD-1340)	

^aLOD indicates the value was below the limit of detection. Unit is parts per trillion by volume (pptv).

the ambient CH₂O mixing ratio, and the total uncertainty for each measurement is determined from the quadrature addition of the LOD with the systematic uncertainty (Fried et al., unpublished manuscript, 2007).

2.2.3. Comparison of CH₂O Measurements

[13] Coincident CH₂O measurements by the URI-USNA group and the NCAR group have occurred on several aircraft missions providing a series of comparison data. During INTEX-NA, URI-USNA CH₂O measurements were approximately 70% of NCAR CH₂O, more in the UT, with a weighted bivariate linear regression yielding an r^2 of 0.89 (Fried et al., unpublished manuscript, 2007). The agreement between URI-USNA and NCAR also improved throughout the INTEX-NA mission. This result is opposite of measurements made during the NASA TRACE-P missions where URI-USNA CH₂O was greater. However, at present we have no explanation for the discrepancy and the apparent change with mission or with time. For a more complete explanation of the instrument comparison see Fried et al. (unpublished manuscript, 2007).

3. Results and Discussion

[14] H₂O₂, CH₃OOH, and CH₂O mixing ratios were measured during three aircraft missions across North America and the North Atlantic covering a broad temporal range. The flight tracks and dates of each mission are shown in Figure 1. Singh et al. [2006], Atlas et al. [2003], and Singh et al. [1999] and Thompson et al. [2000] provide overviews of the INTEX-NA, TOPSE, and SONEX aircraft campaigns, respectively.

3.1. Comparison of H₂O₂, CH₃OOH, and CH₂O During INTEX-NA, TOPSE, and SONEX

[15] The mean and median H₂O₂ measured during INTEX-NA (1390 and 1070 pptv) were about ten times larger than those observed during TOPSE and SONEX (170, 150 and 120, 80 pptv) (Table 1). The higher INTEX-NA mixing ratios are consistent with increased photochemical production during the summer months compared to production during the winter-spring sampling period of TOPSE and the fall sampling period of SONEX. In addition to the time of sampling, the relative locations of each mission impacted the H₂O₂ mixing ratios. INTEX-NA flew over continental regions and along the northeast coast of the United States, often sampling in the BL, while TOPSE sampled at higher latitudes and SONEX sampled a larger portion of UT air. H₂O₂ mixing ratios are typically lower at higher latitudes and higher altitudes and therefore are expected to be lower during TOPSE and SONEX. During INTEX-NA, H₂O₂ ranged from a minimum of LOD (12.5 pptv) to a maximum of 13 ppbv. Previous

studies over the United States during the summer have observed H₂O₂ mixing ratios that ranged by a factor of 10, from ~150 pptv to ~5 ppbv, during the study [Boatman et al., 1990; Daum et al., 1990; Balasubramanian and Husain, 1997; Weinstein-Lloyd et al., 1998]. The high H₂O₂ values measured during INTEX-NA are notable as they are some of the highest observed over North America. However, H₂O₂ values in this range have been encountered before in PEM-West and TRACE-P in Asian outflow [Heikes et al., 1996a; O'Sullivan et al., 2004] and in TRACE-A in Brazilian outflow [Heikes et al., 1996b].

[16] The range of observed H₂O₂ during INTEX-NA is much larger than recorded during TOPSE and SONEX which also measured a minimum value of LOD (25 pptv) but observed maximum H₂O₂ levels of only 1330 pptv and 670 pptv respectively. This most likely reflects the large variability in air mass type encountered during INTEX-NA. The mission sampled heavily polluted outflow from the eastern United States and biomass burning plumes from Alaska, containing elevated H₂O₂, and stratospheric intrusions, containing low H₂O₂. In contrast to INTEX-NA, the air masses sampled during TOPSE and SONEX were more homogeneous in origin.

[17] It has also been observed that during the transition from winter to spring, peroxides become more variable because of changes in atmospheric transport as the polar front moves north [Snow et al., 2003]. Highly variable transport patterns over the United States and decreased photochemical lifetime of peroxides also occur during the summer [Jaeglé et al., 2000; Cantrell et al., 2003] increasing H₂O₂ variability. Furthermore, INTEX-NA was highly influenced by scattered convective activity [Bertram et al., 2006; Fried et al., unpublished manuscript, 2007] in which H₂O₂ was removed by precipitation further increasing its variability. Discussions of cases showing convective transport and long-range transport of biomass burning plumes are found in sections 3.3 and 3.4 of this paper.

[18] During INTEX-NA, H₂O₂ mixing ratios dropped significantly above 6 km (Figure 2a). Median mixing ratios of H₂O₂ were ~2 ppbv in the BL (<1 km) and the middle troposphere (MT, 1–6 km) while above 6 km, the median H₂O₂ dropped to 400 pptv. These observations agree well with other summertime studies conducted over North America [Boatman et al., 1990; Daum et al., 1990; Balasubramanian and Husain, 1997; Weinstein-Lloyd et al., 1998]. The range of H₂O₂ measurements also dropped above 6 km. Below 6 km, H₂O₂ levels ranged from the LOD to above 13 ppbv while above 6 km, the highest H₂O₂ mixing ratio observed was ~5 ppbv. The highest H₂O₂ levels in the UT were observed at lower latitudes with a difference of 8 ppb in the observed maximum between 30 and 50° latitude. These H₂O₂ values are significantly

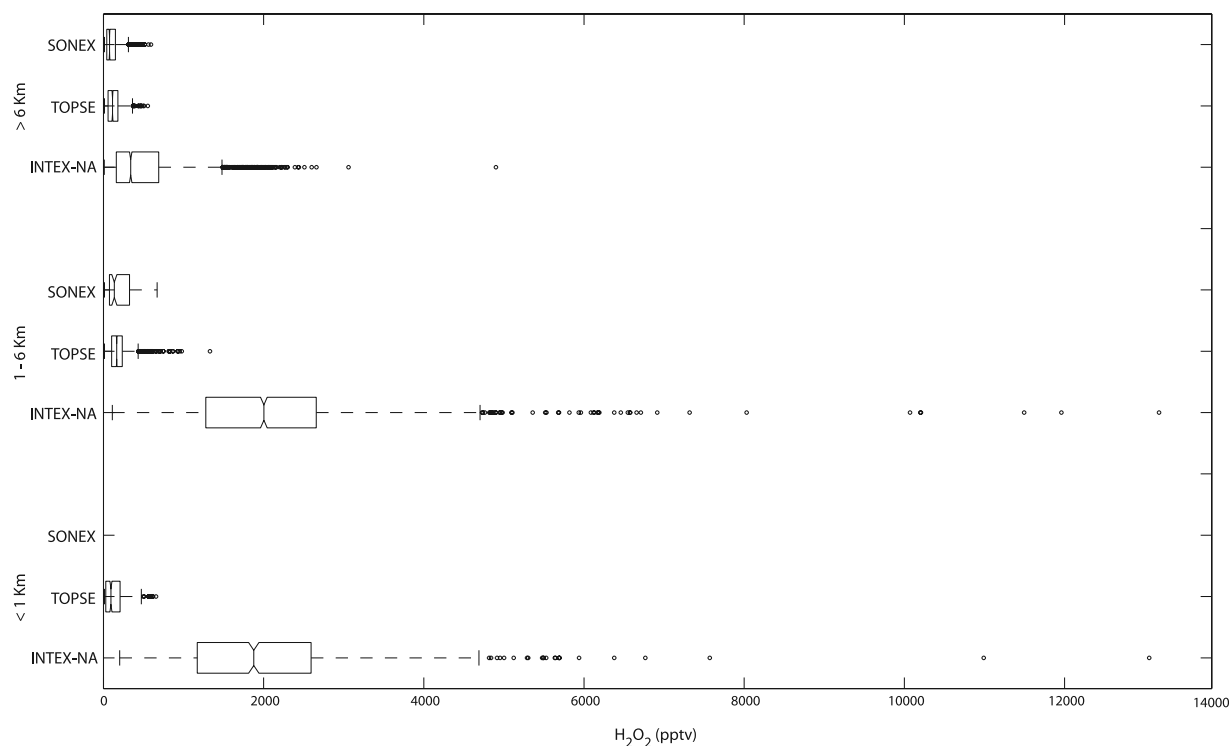


Figure 2a. H₂O₂ mixing ratios during INTEX-NA, TOPSE, and SONEX for three different altitude bins (<1 km, 1–6 km, and >6 km). Each box has lines at the lower quartile, median, and upper quartile values. The whiskers extend to 1.5 times the interquartile range. The notch in the box estimates the uncertainty about the median, and no overlap between the notches indicates a statistical difference between samples at the 95% confidence level.

higher than measurements made during the TOPSE and SONEX missions. During TOPSE and SONEX, maximum H₂O₂ measurements made above 6 km are less than the upper quartile of H₂O₂ measurements made during INTEX-NA. In the MT, H₂O₂ measurements reached 1 ppbv during TOPSE but never exceeded 500 pptv during SONEX. These results are not surprising given the different solar radiation levels during these campaigns and the influence of convection from the BL to the UT.

[19] Regardless of the mission, H₂O₂ levels reach a maximum in the MT. A peak is typically found at ~2 km because of the combined impact of water vapor and solar radiation. This peak has been observed in the tropics [O'Sullivan *et al.*, 1999], the North Pacific [Heikes *et al.*, 1996a], and over continental regions including North America [Boatman *et al.*, 1990; Daum *et al.*, 1990; Heikes, 1992; Ray *et al.*, 1992; Balasubramanian and Husain, 1997; Snow *et al.*, 2003].

[20] CH₃OOH mixing ratios during INTEX-NA were more variable than during TOPSE or SONEX. During all missions, the minimum CH₃OOH mixing ratio measured was LOD and the maximum mixing ratio measured during INTEX-NA, TOPSE, and SONEX were 2150, 1400, and 340 pptv respectively. The relatively small increase in CH₃OOH compared to H₂O₂ over the winter-spring to summer comparison can be explained by the existence of two seasonally dependent peroxide regimes. *de Serve* [1994] and Snow *et al.* [2003] showed an organically dominated peroxide regime, dominated primarily by

CH₃OOH, during the winter-spring when lower sunlight, lower temperatures, and lower water vapor exist. H₂O₂ dominates during the summer when sunlight, temperatures, and water vapor increase. Therefore it is not surprising to find a different transition across this temporal range for CH₃OOH compared to H₂O₂ as is exhibited in the INTEX-NA-TOPSE comparison. Mixing ratios are much lower during SONEX because of the location of that mission; the majority of flights occurred in the UT [Singh *et al.*, 1999; Thompson *et al.*, 2000], where CH₃OOH is significantly lower when not perturbed by convection.

[21] CH₃OOH mixing ratios showed a slight decrease with altitude during INTEX-NA (Figure 2b). Median mixing ratios in the BL were ~630 pptv and decreased to 600 pptv in the MT and to 200 pptv above 6 km. BL mixing ratios are lower than those observed by Weinstein-Lloyd *et al.* [1998] who found ~1–2 ppbv CH₃OOH between 0 and 3 km during the summer over urban and agricultural land in the Nashville region. The decrease with altitude is also unlike the TOPSE mission, where CH₃OOH mixing ratios above 6 km exceeded those in the MT and the UT median for INTEX-NA. Snow *et al.* [2003] attributed the elevated CH₃OOH mixing ratios to the transport of subtropical marine air containing high levels of CH₃OOH. Even with the transport of subtropical marine air during TOPSE, this result is somewhat surprising given the differences in solar radiation between these two missions. As with H₂O₂, the range of INTEX-NA BL and MT CH₃OOH measurements was larger than that observed in the UT; BL and MT

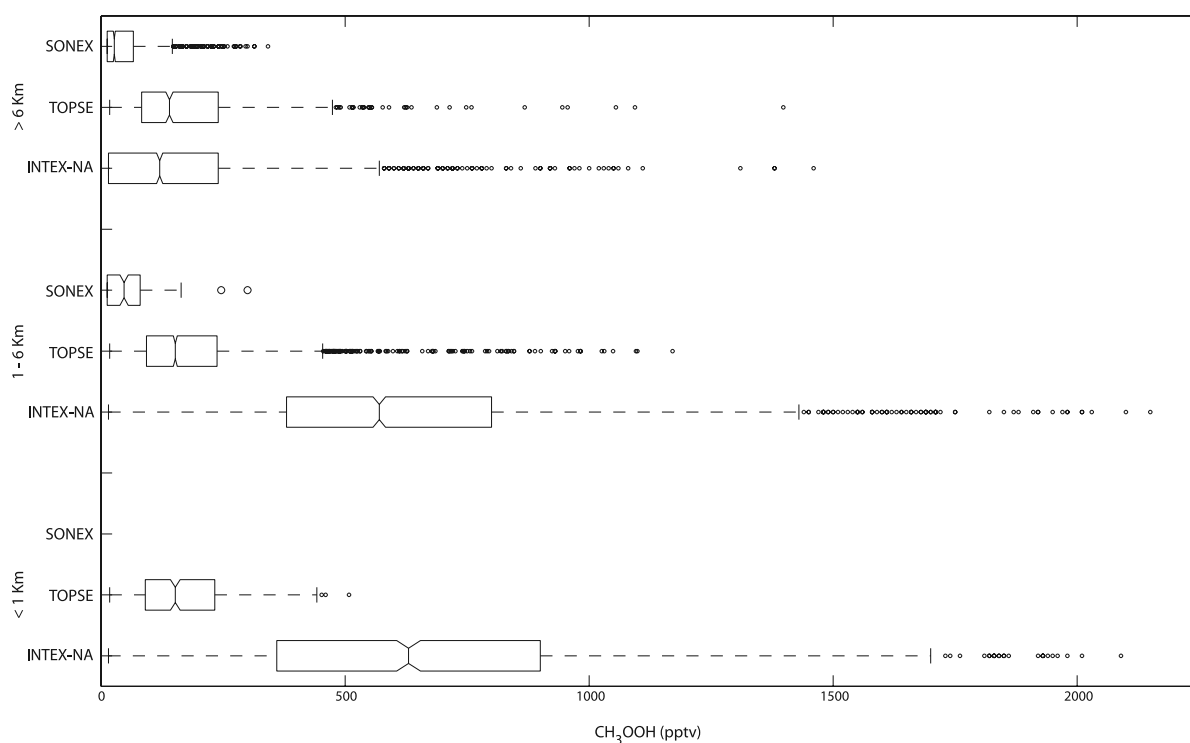


Figure 2b. CH₃OOH mixing ratios during INTEX-NA, TOPSE, and SONEX for three different altitude bins (<1 km, 1–6 km, and >6 km). Each box has lines at the lower quartile, median, and upper quartile values. The whiskers extend to 1.5 times the interquartile range. The notch in the box estimates the uncertainty about the median, and no overlap between the notches indicates a statistical difference between samples at the 95% confidence level.

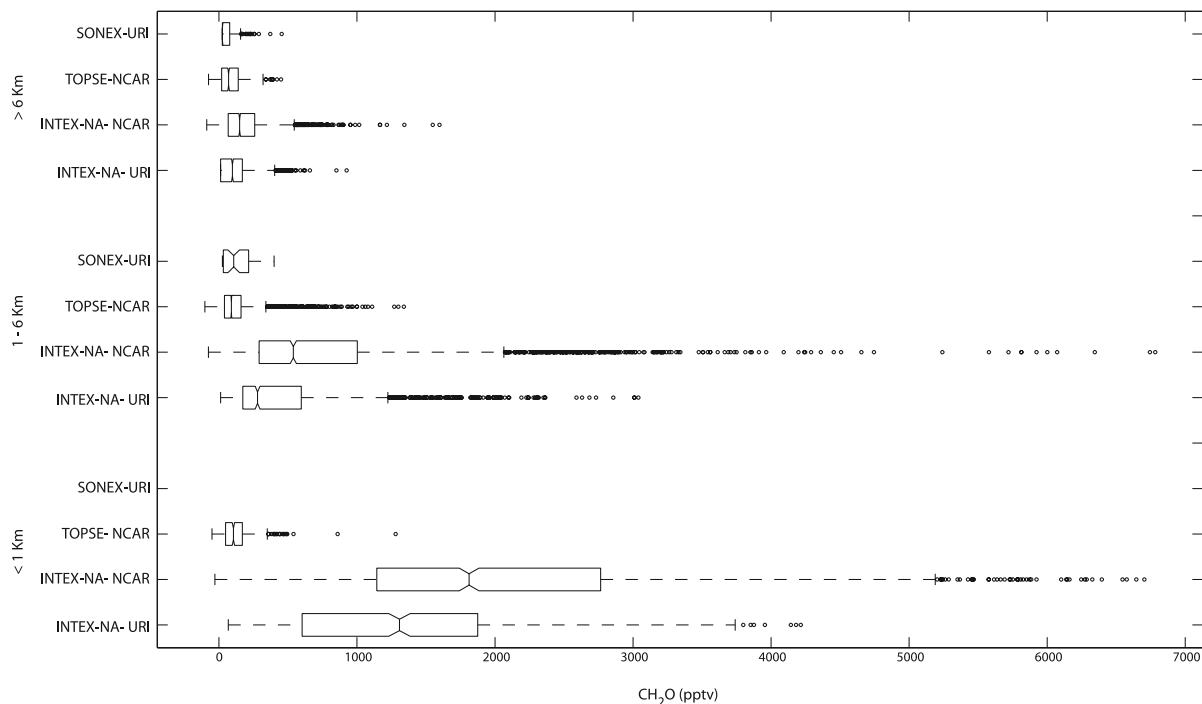


Figure 2c. CH₂O mixing ratios during INTEX-NA, TOPSE, and SONEX for three different altitude bins (<1 km, 1–6 km, and >6 km). CH₂O measurements were made by URI-USNA and NCAR and the appropriate group is indicated along the y axis. Each box has lines at the lower quartile, median, and upper quartile values. The whiskers extend to 1.5 times the interquartile range. The notch in the box estimates the uncertainty about the median, and no overlap between the notches indicates a statistical difference between samples at the 95% confidence level.

Table 2. Mean/Median and Number of Samples (n) of H₂O₂/CH₃OOH for Three Altitude Bins During INTEX-NA, TOPSE, and SONEX^a

	INTEX-NA	TOPSE	SONEX
<1 km	3.6/3.4 (1639)	0.9/0.7 (1358)	
1–6 km	3.6/3.5 (3547)	1.7/1.1 (6391)	5.4/3.4 (159)
>6 km	5.0/3.5 (4175)	1.4/0.7 (2143)	3.9/2.8 (1693)

^aThe low ratio observed in the boundary layer during TOPSE is most likely due to the dominance of CH₃OOH during the low light and temperature conditions of that high-latitude mission. The upper troposphere peroxide ratio is similar to the boundary layer ratio during INTEX-NA and TOPSE indicating convective activity.

CH₃OOH measurements ranged from the LOD to ~2.5 ppbv while UT measurements were from the LOD to ~1.5 ppbv.

[22] Measurements of CH₃OOH over marine regions compared to those over continental regions yielded a significant difference during INTEX-NA. Mean and median CH₃OOH over marine regions were ~20% greater than measurements made over the North American continent in the BL and UT. This could be a result of continental outflow, however observations of enhanced H₂O₂ and CH₂O were not observed over marine regions. In fact, the opposite observation was made; H₂O₂ and CH₂O were elevated over the North American continent and decreased over marine regions (Fried et al., unpublished manuscript, 2007).

[23] It is important to note that CH₂O was measured by two techniques. The two CH₂O techniques were used simultaneously only on INTEX-NA; CH₂O was measured by NCAR on TOPSE and by URI-USNA on SONEX. For ease of discussion, when referring to CH₂O measurements made during INTEX-NA, the authors will be referring to the URI-USNA measurements unless otherwise noted by the NCAR designation.

[24] The comparison of CH₂O between field missions is similar to that of CH₃OOH with a larger range of mixing ratios observed during INTEX-NA; about a 4 ppbv range on INTEX-NA compared to ~1 ppbv on TOPSE and ~400 pptv on SONEX. Nearly an order of magnitude difference was observed between the CH₂O mean and median during INTEX-NA (480 and 210 pptv) compared to SONEX (70 and 30 pptv). Mean and median CH₂O mixing ratios measured on INTEX-NA are higher by a factor of 3–4, but within an order of magnitude of those sampled on TOPSE (120 pptv and 90 pptv). During INTEX-NA, CH₂O decreased sharply above the BL dropping from a median of 1300 pptv to 600 pptv in the MT and 100 pptv in the UT (Figure 2c). These observations are about a factor of

3 higher than measurements made over the North Atlantic during the September NARE campaign [Fried et al., 2002]. This is also in contrast to TOPSE which had a slight peak in CH₂O mixing ratios in the MT. In all three campaigns, the lowest observed CH₂O levels were found in the UT. The variability in CH₂O also decreased with altitude during all three missions. INTEX-NA observed the largest variability in CH₂O mixing ratios ranging from LOD to 4200 pptv in the BL, LOD to 3100 pptv in the MT and LOD to 1800 pptv in the UT. In contrast, SONEX observed the smallest variability with ranges from LOD to 500 pptv in the MT and LOD to 700 pptv in the UT. The range and magnitude of CH₂O observed on INTEX-NA is similar to measurements at surface sites over North America during the summer [Macdonald et al., 2001; Li et al., 2004] where variability and mixing ratios were controlled by regional meteorology and diurnal photochemical production. The effect of photochemical production is also clearly seen by the latitudinal distribution of CH₂O during INTEX-NA; CH₂O mixing ratios decreased by half from 30 to 50°N.

3.2. Convective Influence in the Upper Troposphere

3.2.1. Peroxide Ratio (H₂O₂/CH₃OOH)

[25] Convective events throughout the world have been identified by using the ratio of H₂O₂ to CH₃OOH [Heikes et al., 1996a; O'Sullivan et al., 1999; Snow et al., 2003]. Peroxides are generally higher in the BL than in the UT [Heikes et al., 1996a] making them excellent indicators of convective outflow. Furthermore, H₂O₂ is preferentially removed during convective events because of its high solubility in water, followed by precipitation or reaction with dissolved sulfur dioxide (SO₂). Cohan et al. [1999] estimated scavenging of H₂O₂ in deep convection was at least 60%. The removal of CH₃OOH during such events is negligible [Heikes et al., 1996a; Pickering et al., 1996; Cohan et al., 1999]. Therefore the H₂O₂/CH₃OOH ratio can be an excellent indicator of convection. O'Sullivan et al. [1999] observed ratios of <1 associated with the Inter Tropical Convergence Zone (ITCZ) and South Pacific Convergence Zone (SPCZ), between altitudes of 8 and 12 km, an indication CH₃OOH had been transported to the UT. Similar values were observed by Pickering et al. [1996] and were associated with tropical convection over Brazil. Snow et al. [2003] observed ratios of <3 associated with the transport of subtropical air to the central United States. The effectiveness of the H₂O₂/CH₃OOH ratio as a convective tracer is lost in ~3 days because the lifetime of CH₃OOH is on the order of 1 to 2 days in the tropics, and slightly longer at higher latitudes [Cohan et al., 1999],

Figure 3. (a) Using the ratio of H₂O₂/CH₃OOH < 1 and O₃ < 100 ppbv as a definition of convective influence (CI) and the H₂O₂/CH₃OOH ratio >3 and O₃ < 100 ppbv as an indicator of free troposphere (FT) air, a comparison of soluble gases, H₂O₂ and HNO₃, in CI and FT measurements above 6 km is shown. Each box has lines at the lower quartile, median, and upper quartile values. The whiskers extend to 1.5 times the interquartile range. The notch in the box estimates the uncertainty about the median, and no overlap between the notches indicates a statistical difference between samples at the 5% significance level. (b) Using the ratio of H₂O₂/CH₃OOH < 1 and O₃ < 100 ppbv as an indicator of convective influence (CI) and the H₂O₂/CH₃OOH ratio >3 and O₃ < 100 ppbv as an indicator of free troposphere (FT) air, a comparison of less soluble gases in CI and FT measurements above 6 km is shown. Each box has lines at the lower quartile, median, and upper quartile values. The whiskers extend to 1.5 times the interquartile range. The notch in the box estimates the uncertainty about the median, and no overlap between the notches indicates a statistical difference between samples at the 5% significance level.

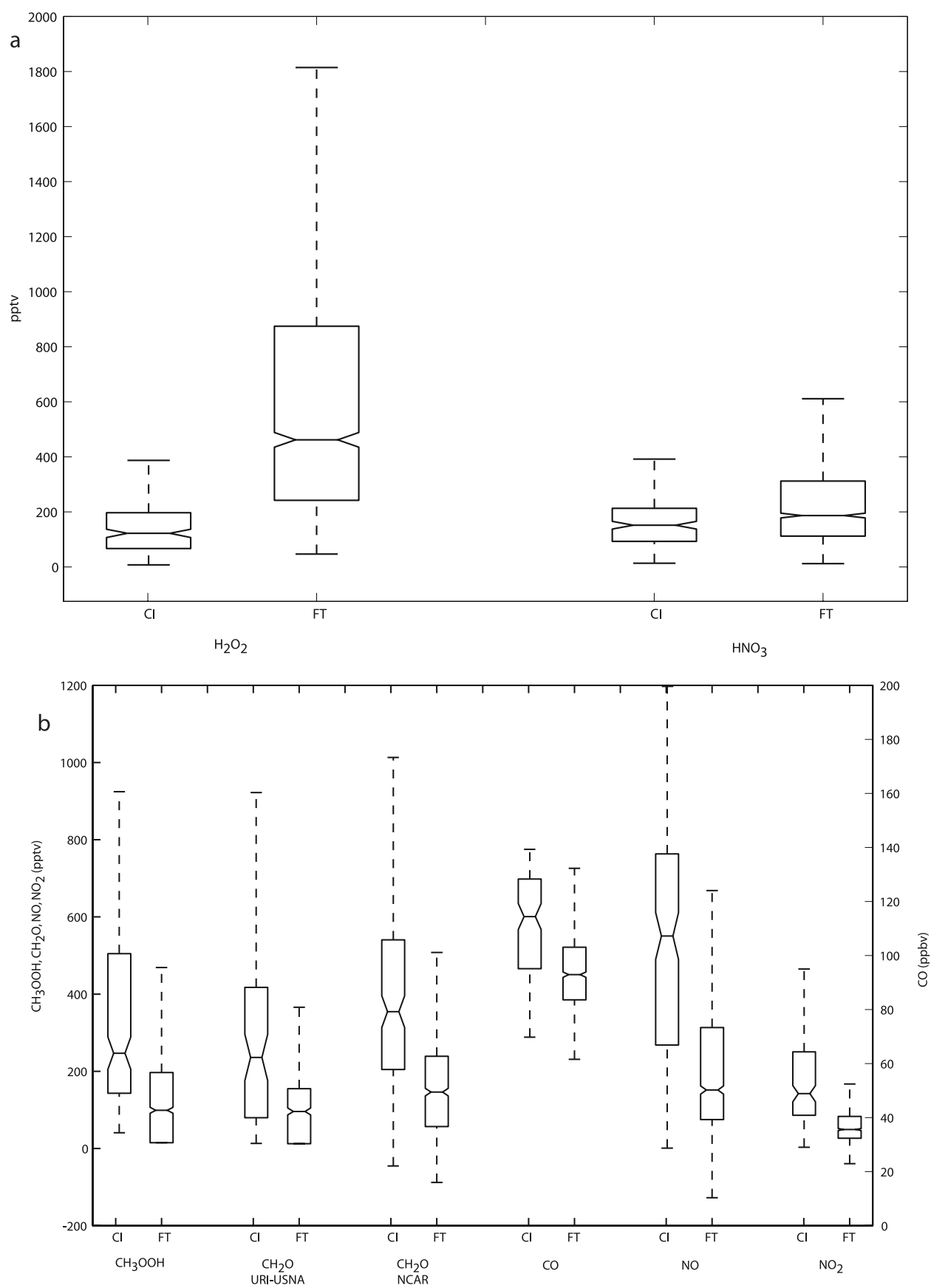


Figure 3

Table 3. Median Mixing Ratios of Key Species in Air Masses Diagnosed as Convectively Influenced (H₂O₂/CH₃OOH < 1 and O₃ < 100) and in Those Air Masses Designated as Free Troposphere (H₂O₂/CH₃OOH > 3 and O₃ < 100)^a

	INTEX-NA	Other Studies					
		SONEX Snow ^b	Jaeglé ^c	TOPSE Snow ^d	Browell ^e	Cohan ^f	Board ^g
<i>Convectively Influenced</i>							
O ₃	72	49	47	25	16	27	33
CO	115	88		100	49	57	57
C ₂ H ₂ /CO	0.95	1.0			0.25	0.6	0.71
C ₂ Cl ₄	3.5	3.6			1.23		
CH ₂ Cl ₂	23.8	24.6					
CH ₃ I	0.08	0.21	>0.25		0.16	0.15	0.08
CHBr ₃	0.39	0.80	0.98		0.59	0.76	0.41
H ₂ O ₂ /CH ₃ OOH	0.55	1.3		<0.5		0.66	1.3
Relative humidity	82	25	75		52	82	
<i>Free Troposphere</i>							
O ₃	75	58		~50	24	51	
CO	93	80		~120	46	64	
C ₂ H ₂ /CO	0.80	1.0			0.33	0.9	
C ₂ Cl ₄	3.1	2.9			1.36		
CH ₂ Cl ₂	22.7	23.9					
CH ₃ I	0.05	0.11			0.13	0.05	
CHBr ₃	0.35	0.49			0.52	0.33	
H ₂ O ₂ /CH ₃ OOH	4.9	1.7		>1		2.5	
Relative humidity	42	11			43	13	

^aResults from previous studies in the tropical Pacific troposphere, North American troposphere, and North Atlantic troposphere are shown. Mixing ratios are shown in parts per trillion by volume (pptv) except for CO and O₃ which are in parts per billion by volume (ppbv) and relative humidity which is shown in %.

^bSnow [2002] (SONEX: North Atlantic troposphere).

^cJaeglé et al. [2000] (North Atlantic troposphere).

^dSnow et al. [2003] (TOPSE: subtropical air over North America).

^eBrowell et al. [2001].

^fCohan et al. [1999].

^gBoard et al. [1999] (tropical Pacific troposphere).

making the H₂O₂/CH₃OOH ratio uniquely suited for detecting recent convection.

[26] Table 2 shows the mean and median H₂O₂/CH₃OOH ratio in the BL, MT, and UT during INTEX-NA, TOPSE, and SONEX. The median peroxide ratio during TOPSE (0.7) was driven below 1 by the dominance of organic peroxides during the cold, dark winter periods [Snow et al., 2003]. The mean BL H₂O₂/CH₃OOH ratio poleward of 50°N in March was 0.7 indicating a strong dominance of CH₃OOH. The ratio reached 1.2 by May but never exceeded 1.5 suggesting an increase in H₂O₂ due to increased solar radiation and a decrease in CH₃OOH due to a decrease in hydrocarbon mixing ratios at lower altitudes [Blake et al., 2003]. During INTEX-NA, the median BL H₂O₂/CH₃OOH ratio was 3.4. This indicates a peroxide regime dominated by H₂O₂. This also agrees well with de Serves [1994] who found a shift from an organic peroxide dominated to H₂O₂ dominated atmosphere when temperature and solar radiation increased.

[27] In the MT the median INTEX-NA H₂O₂/CH₃OOH ratio was 3.5, similar to the MT ratio observed during SONEX (3.4). An increase in the MT ratio was also observed during TOPSE although the ratio was still much lower, ~1. During TOPSE and SONEX, the median H₂O₂/CH₃OOH ratio decreased in the UT, suggesting some convective influence, but remained constant during INTEX-NA. The INTEX-NA UT ratio is surprisingly high given Bertram et al. [2006] estimated 30–56% of the atmosphere sampled during INTEX-NA had been cloud processed within the past two days, which is an indication

of strong convective activity and would suggest removal of H₂O₂. However, it is possible that the UT H₂O₂/CH₃OOH ratio is being driven by local photochemistry. Crawford et al. [1999] suggest local photochemistry driven by high H₂O (666 ppmv) in tropical convective outflow, not convective transport itself, may be the most important factor in UT H₂O₂ variability. During INTEX-NA, however, the UT conditions were drier (median UT H₂O was 340 ppmv) and therefore would result in less photochemical production of HO_x, leading to lower H₂O₂. Another important factor is the low UT SO₂ observations (median UT SO₂ ~24 pptv), making heterogeneous removal of H₂O₂ by SO₂ small. In actuality, transport, local photochemical production, and heterogeneous reactions are most likely all factors controlling the UT H₂O₂/CH₃OOH ratio over North America.

3.2.2. Convective Enhancements During INTEX-NA

[28] Convective influence (CI) in the UT was defined as the H₂O₂/CH₃OOH ratio <1 and O₃ < 100 ppbv (to exclude stratospheric samples). The cut off point of 1 is consistent with other studies that have used the peroxide ratio to identify convection [Heikes et al., 1996a; O'Sullivan et al., 1999; Snow et al., 2003]. The distribution of the INTEX-NA H₂O₂/CH₃OOH ratio in the BL was used to determine the ratio for free unperturbed UT (FT) as the H₂O₂/CH₃OOH ratio >3 and O₃ < 100, ppbv above 6 km. Note that the definition of FT for this study means those samples not influenced by recent convection (within 3–4 days) or by the stratosphere. Using this definition of CI and FT, a comparison of soluble and less soluble species are presented in Figures 3a and 3b. The mean H₂O₂ and HNO₃

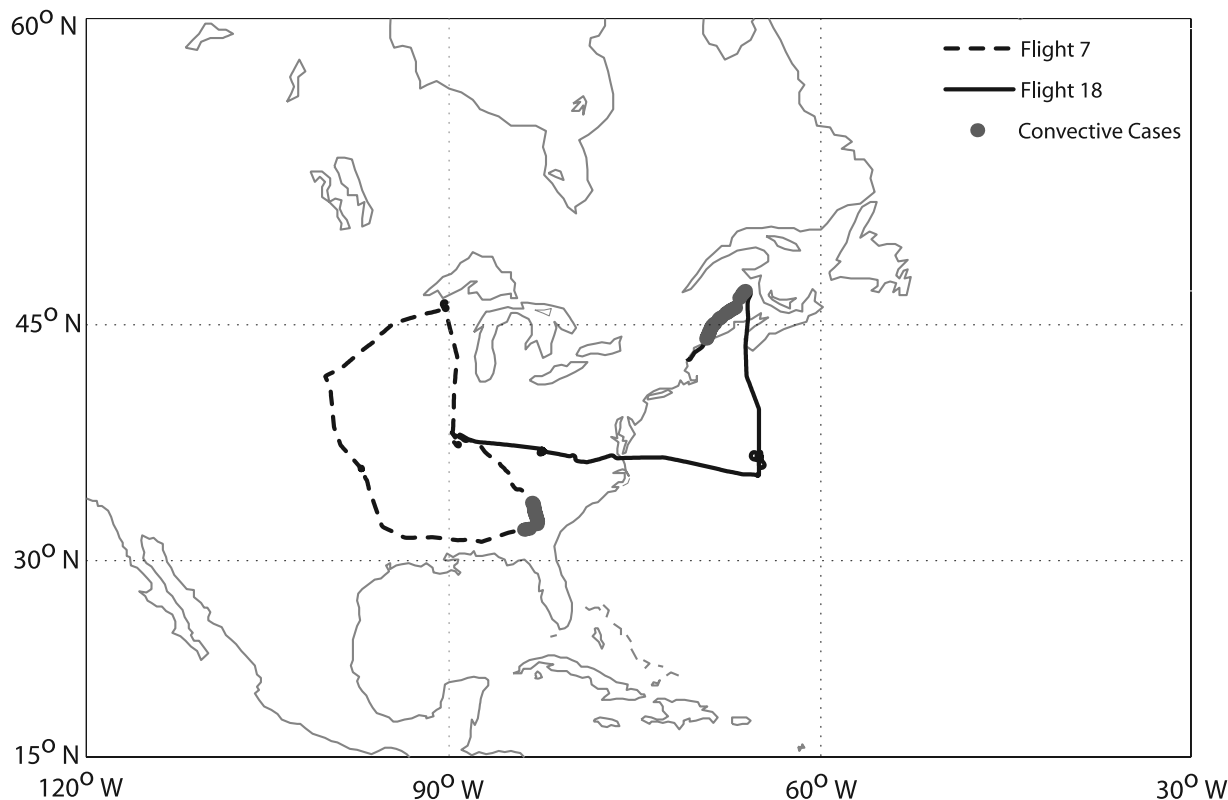


Figure 4. Flight tracks of flight 7 and flight 18 showing the regions of convectively influenced air highlighted with shaded dots.

levels in CI samples are lower than those samples identified as FT, the difference is statistically significant at the 95% confidence level. Soluble species such as H₂O₂ and HNO₃ are removed during the convective process through precipitation and cloud processing [Cohan *et al.*, 1999; O'Sullivan *et al.*, 1999] and the lower mixing ratio found in CI samples is expected. In contrast, less soluble species, such as CH₃OOH and CO, show a statistically higher mean in the CI samples than in the FT samples (Figure 3b) providing evidence of the UT enhancement of CH₃OOH via convective outflow. The difference between the mean of the two sample groups is significant at the 95% confidence level. With a lifetime of ~2 months [Warneck, 2000], CO is expected to be well mixed in the UT. However, given the peroxide ratio method detects fresh convection and most of the INTEX-NA storms occurred over the eastern United States where BL CO is highly elevated, it is not surprising to see a statistically higher median in CI samples compared to FT. Pooled URI-USNA and NCAR CH₂O observations were high in CI samples compared to FT samples. It is worth noting that the CH₂O increase between the CI and FT time periods is much larger in measurements acquired by the NCAR group. Lightning, an UT source of NO_x [Luke *et al.*, 1992], or anthropogenic emissions, a BL source of NO_x, are most likely responsible for the elevated levels of NO_x observed in the CI samples.

[29] Table 3 presents a comparison of CI air masses to FT air masses during aircraft campaigns over different regions. In general INTEX-NA measured relatively high O₃, CO, C₂Cl₄, and CH₂Cl₂ in CI samples compared to other studies. This is most likely due to the location of sampling; INTEX-NA

sampled over continental regions where BL mixing ratios are higher than over marine regions. CH₃I and CHBr₃ were comparably lower during INTEX-NA, most likely due to the lack of marine influence on the convective outflow compared to the other aircraft missions, which took place over the Atlantic and Pacific Oceans.

3.3. Evidence of Convective Outflow: A Case Study of INTEX-NA Flights 7 and 18

[30] Although convective influence was detected throughout the UT over North America and along the eastern coast during INTEX-NA, flights 7 and 18 present especially clear cases demonstrating the influence of convection on peroxides and CH₂O in the UT. Figure 4 shows the flight tracks of flights 7 and 18. Flight 7 occurred on 12 July and flew over the central United States and sampled fresh convective outflow along the southeastern leg of the flight over the southeastern United States. This region was dominated by a high-pressure system located over the northern Gulf of Mexico, just to the south of the flight track. The anticyclonic flow of this dominant system produced onshore southerly winds along the western Gulf coast and offshore northerly winds along the eastern Gulf coast. High-pressure conditions are typically associated with subsiding air and are not associated with significant convective activity. However, on 12 July, the winds were light, ranging from 5–20 knots at 3 km to ~20 knots at 10 km. The light UT winds, in particular, resulted in little movement of air previously lifted into the UT by convection up to 3 days earlier. Figure 5 shows the pathway of convected air parcels and potential convection cells on a GOES water vapor image taken 36 hours prior to sampling.

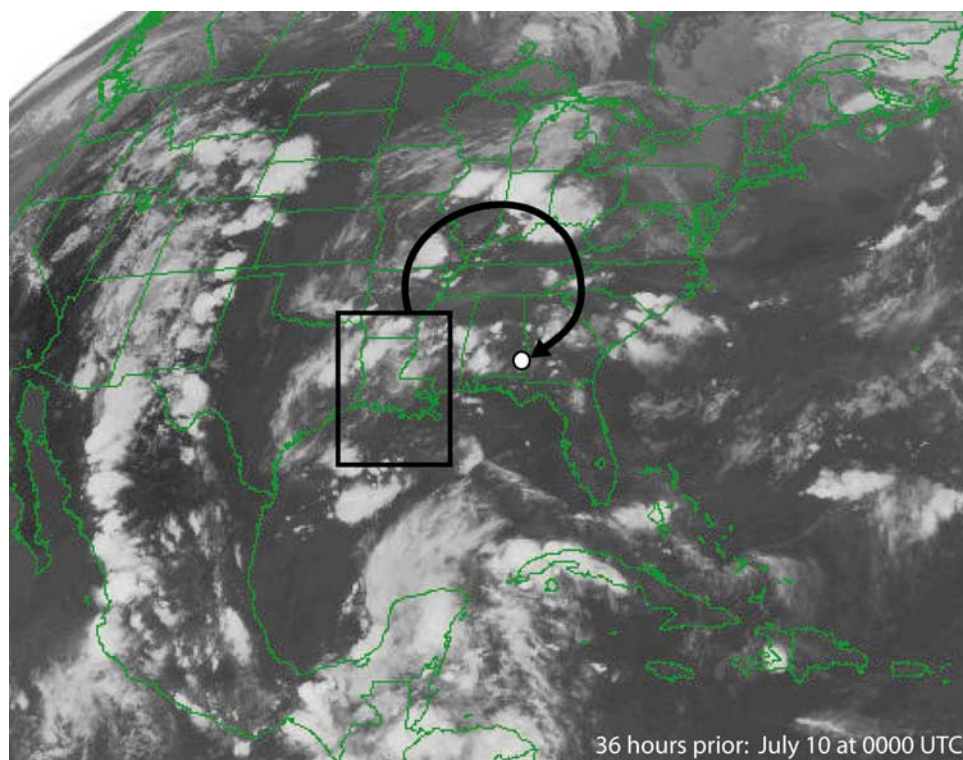


Figure 5. GOES water vapor image for 10 July at 0000 UTC, approximately 36 hours prior to the sampling of aged convective outflow on 12 July. The dark black line indicates the direction air masses moved between the GOES image and the time of the convective sampling. Possible convective cells that may have contributed to the aged outflow sampled during flight 7 are highlighted in the black box. The location where convective influenced air was sampled on flight 7 is shown as a white dot outlined in black.

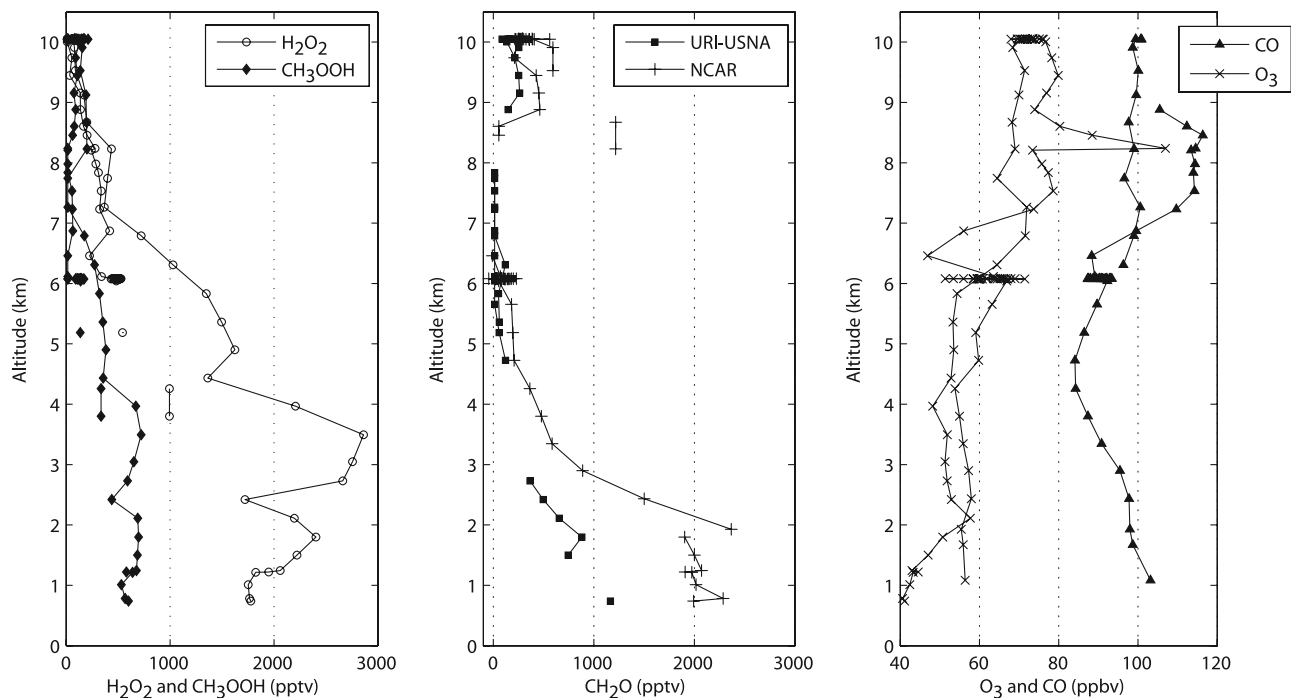


Figure 6. Vertical profiles of H₂O₂, CH₃OOH, CH₂O, O₃, and CO for flight 7. Elevated CH₃OOH, CH₂O, O₃, and CO in the upper troposphere is indicative of convective lofting of boundary layer air. H₂O₂ is preferentially removed by precipitation because of its high solubility.

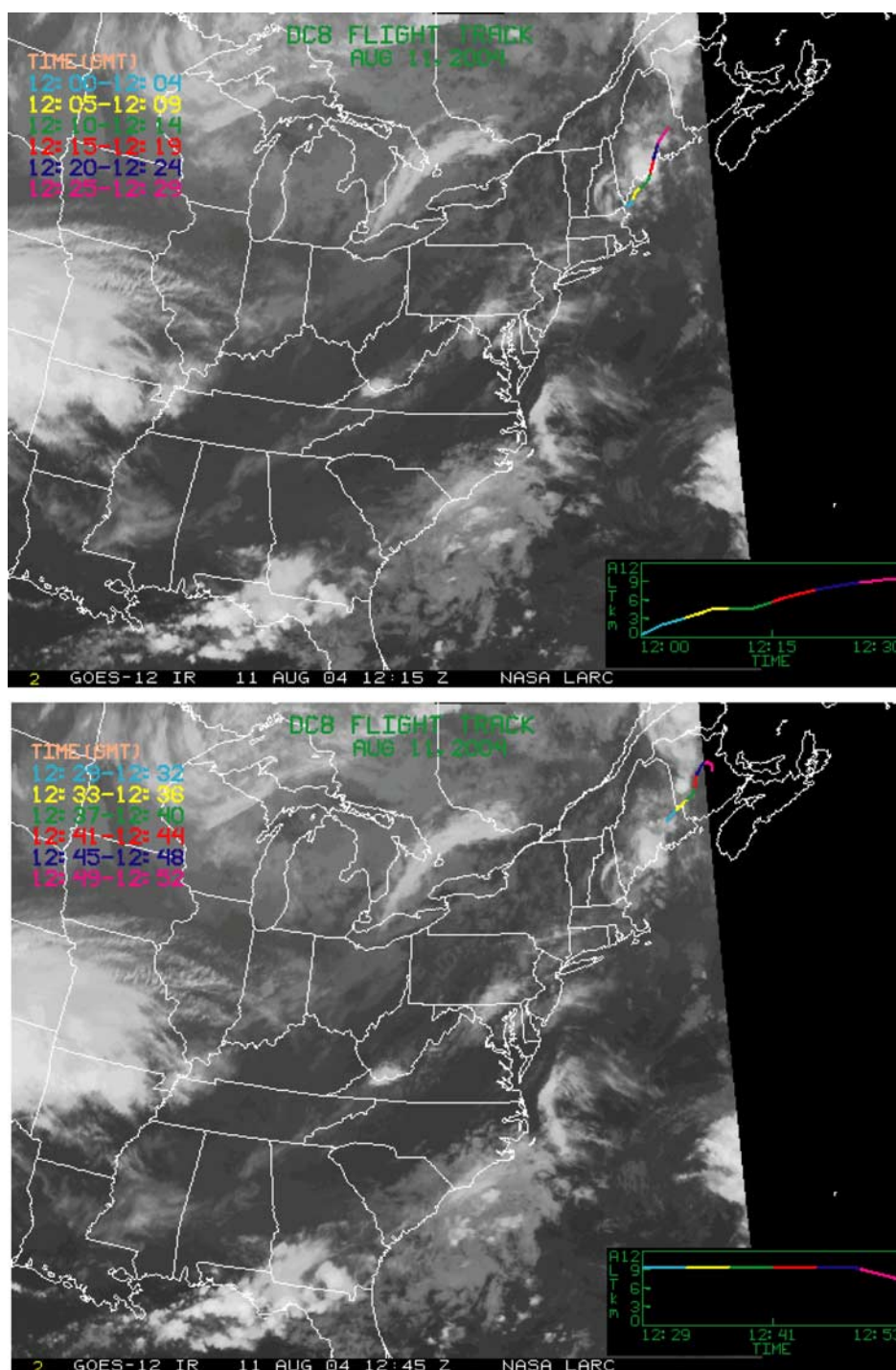


Figure 7. Flight track, where convective outflow was sampled, is overlaid onto a GOES water vapor image. (top) First half of the flight track and (bottom) second half. Both images show the aircraft flew very near a convective cell just upwind, to the south/southwest of the flight track.

Using this meteorological analysis, the age of the convective outflow is determined to be ~ 3 days. The lifetime of CH₃OOH in the summer troposphere is ~ 3 days, within the age of this convected plume.

[31] Figure 6 shows an altitude profile collected as the aircraft approached the convective outflow. Both H₂O₂ and CH₃OOH exhibited the typical decrease with altitude.

However, above 8 km, H₂O₂ continued to decrease while CH₃OOH showed a slight enhancement of ~ 200 pptv. The CH₃OOH enhancement is a result of BL air, convectively lifted and transported to the UT while the same process subsequently removed H₂O₂. CH₂O is enhanced above 8 km and reaches 600 pptv compared to 50 pptv observed between 5 and 8 km. Because the lifetime of CH₂O is

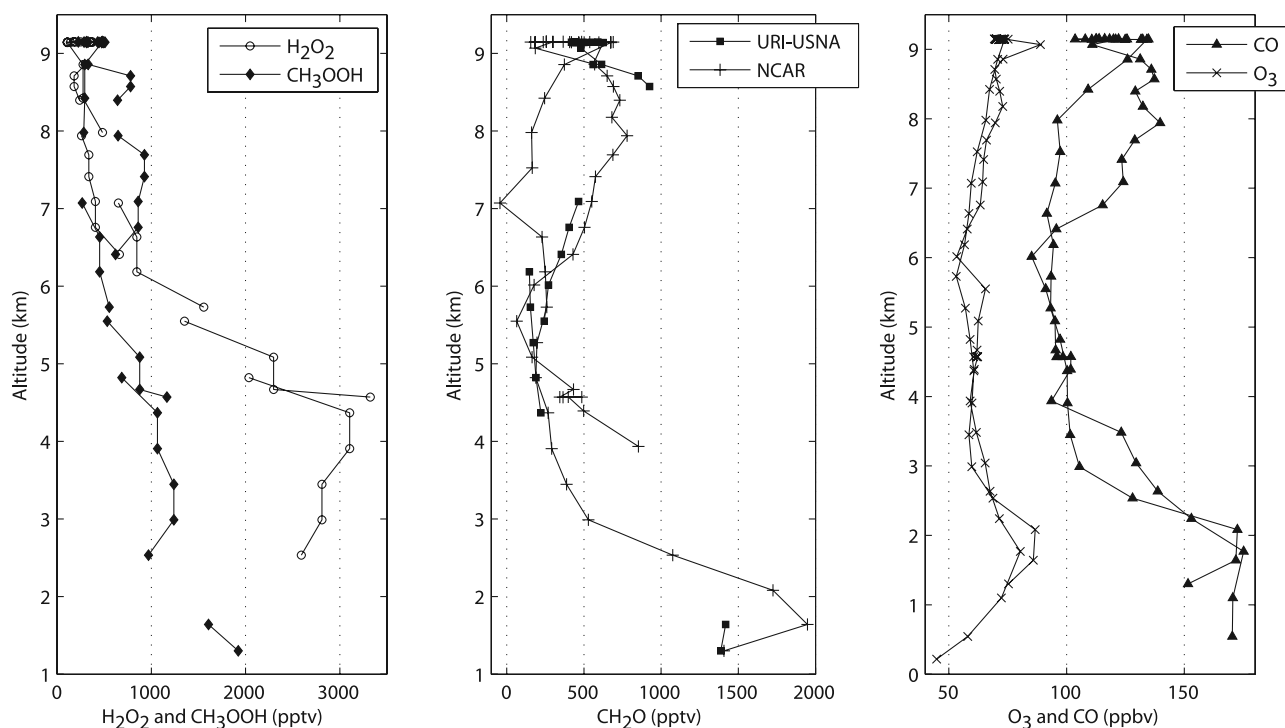


Figure 8. Vertical profiles of H₂O₂, CH₃OOH, CH₂O, O₃, and CO for flight 18. Elevated CH₃OOH, CH₂O, O₃, and CO above 6 km suggests convective outflow of boundary layer air. H₂O₂ is preferentially removed by precipitation because of its high solubility.

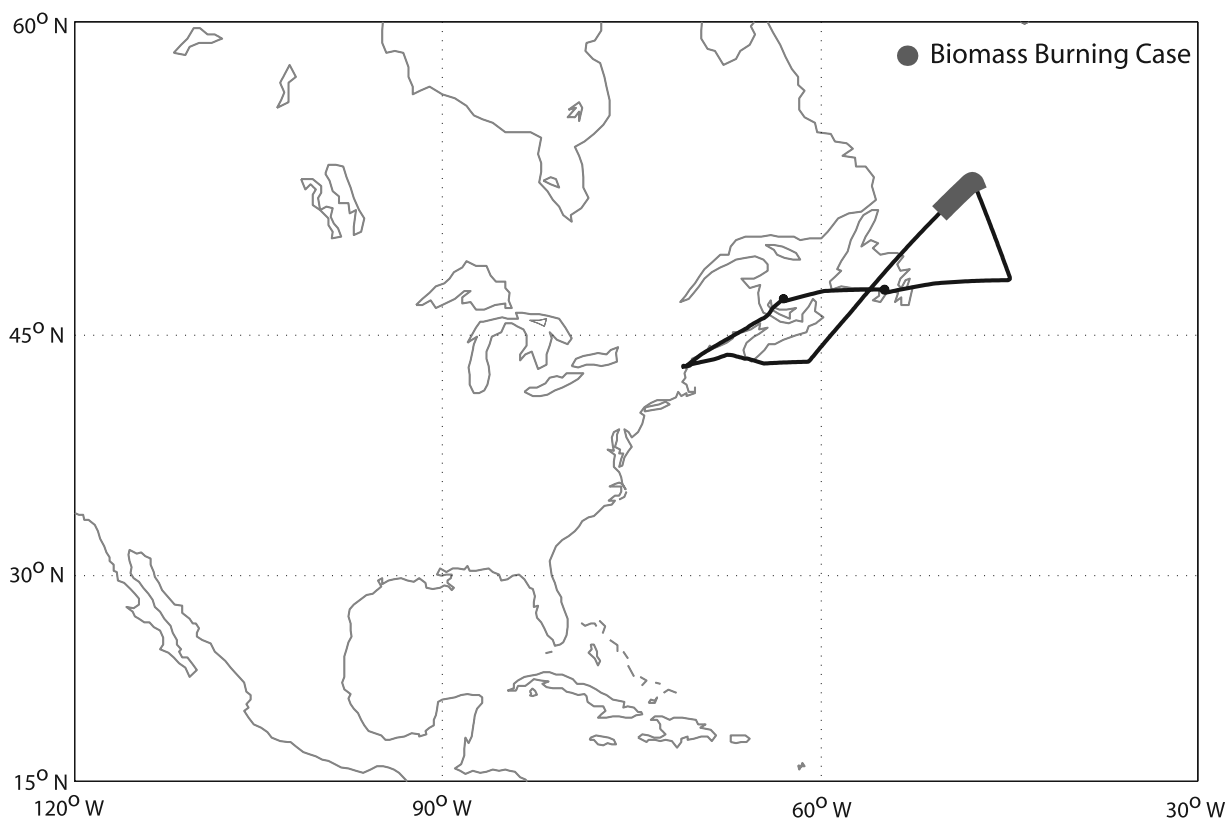


Figure 9. Flight 9 flight track showing the location of the Alaskan fire plume with shaded dots.

FSU Meteorology FLT Level, 120 Hour Trajectories for Leg 26
 INTEX-B DC8 Flight on 18 Jul 2004

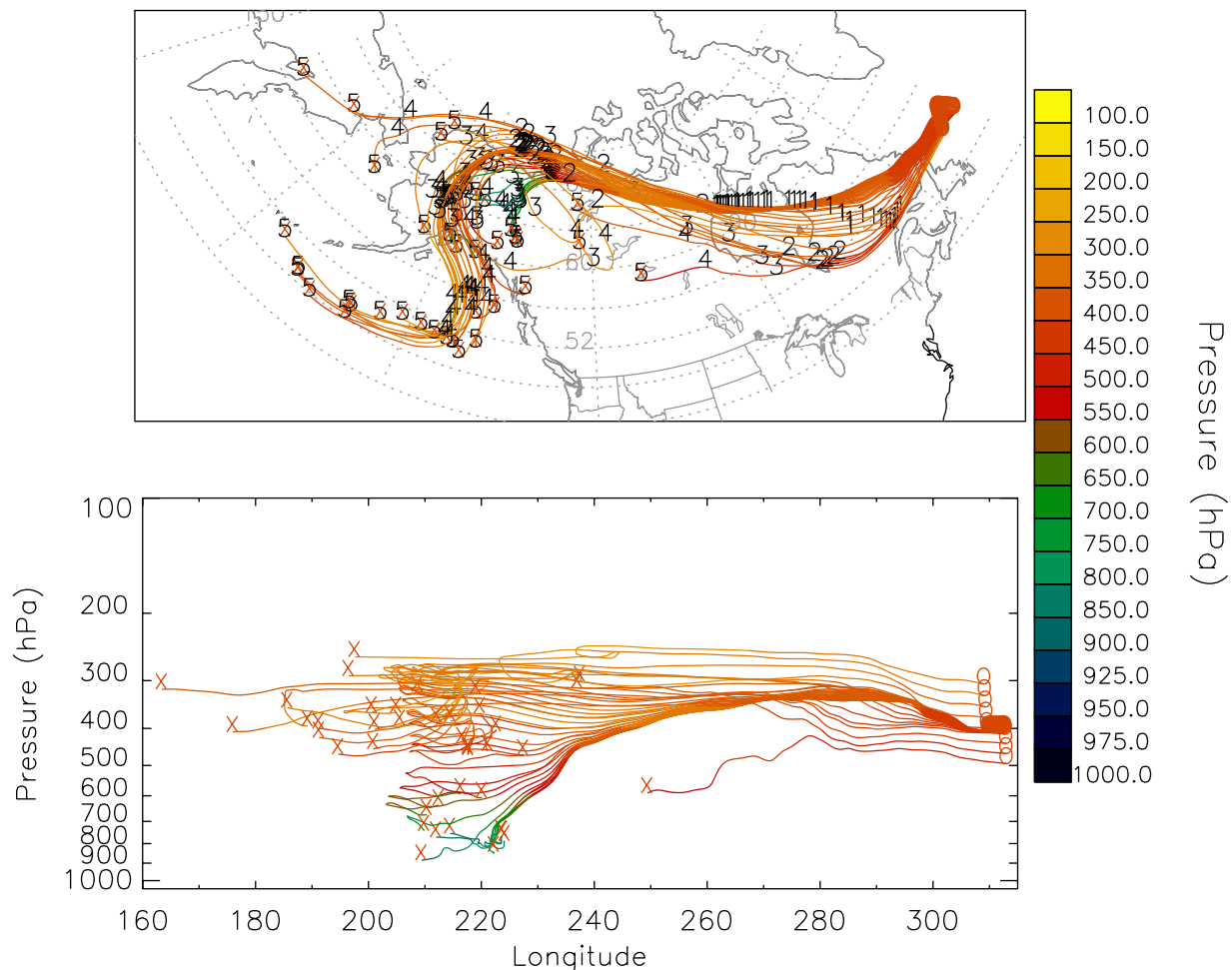


Figure 10. Air mass back trajectories showing strong westerly flow originating over Alaska 5 days prior to flight 9.

several hours during sunlit conditions, these CH₂O enhancements are an indication of the photochemical production from reactive hydrocarbons and reflect the vertical transport of the hydrocarbons. Fried et al. (unpublished manuscript, 2007) provide a detailed discussion of the photochemical production of CH₂O within convective outflow. O₃, CO, and relative humidity (RH) also increase in the UT; O₃ averages ~70 ppbv above 8 km but CO, which peaks at 115 ppbv, begins to decrease around 8.5 km. RH increased to >80% above 8 km providing further evidence that convective outflow was sampled. This event contrasts enhanced UT CH₃OOH cases during TOPSE which were a result of the transport of subtropical marine air that was relatively clean with low CO (100 ppbv) and O₃ (25 ppbv) and suggests convection over North America plays an important role in increasing UT CH₂O precursors, O₃, and possibly CO.

[32] Flight 18 made two distinct legs, one south across the western N. Atlantic and the other across the coastal waters of the eastern United States toward the central United States

(Figure 4). Convective outflow was sampled at the beginning of the flight, as the aircraft headed north over New Brunswick. The dominant meteorological features were an occluded and a cold front extending south of a well-developed low-pressure system just north of the Great Lakes. East of the cold front, relatively warm air (surface temperatures were ~70 F) moved to the north along the eastern seaboard while west of the cold front, relatively cold air (surface temperatures were ~60 F) shifted from northwesterly to southwesterly flow following the cyclonic motion of the low pressure. Cold fronts are typically associated with convective activity and on 11 August, convective activity was scattered across the eastern seaboard ahead of the cold front. Figure 7 shows the flight track over a GOES water vapor image taken at the time of sampling. Convective storm cells, just upwind of the CI sampled air, are visible on these images. The convective outflow sampled during this flight was ~4 hours old and was characterized by ~100% RH and 100% cloudiness, indicating we flew through active convection.

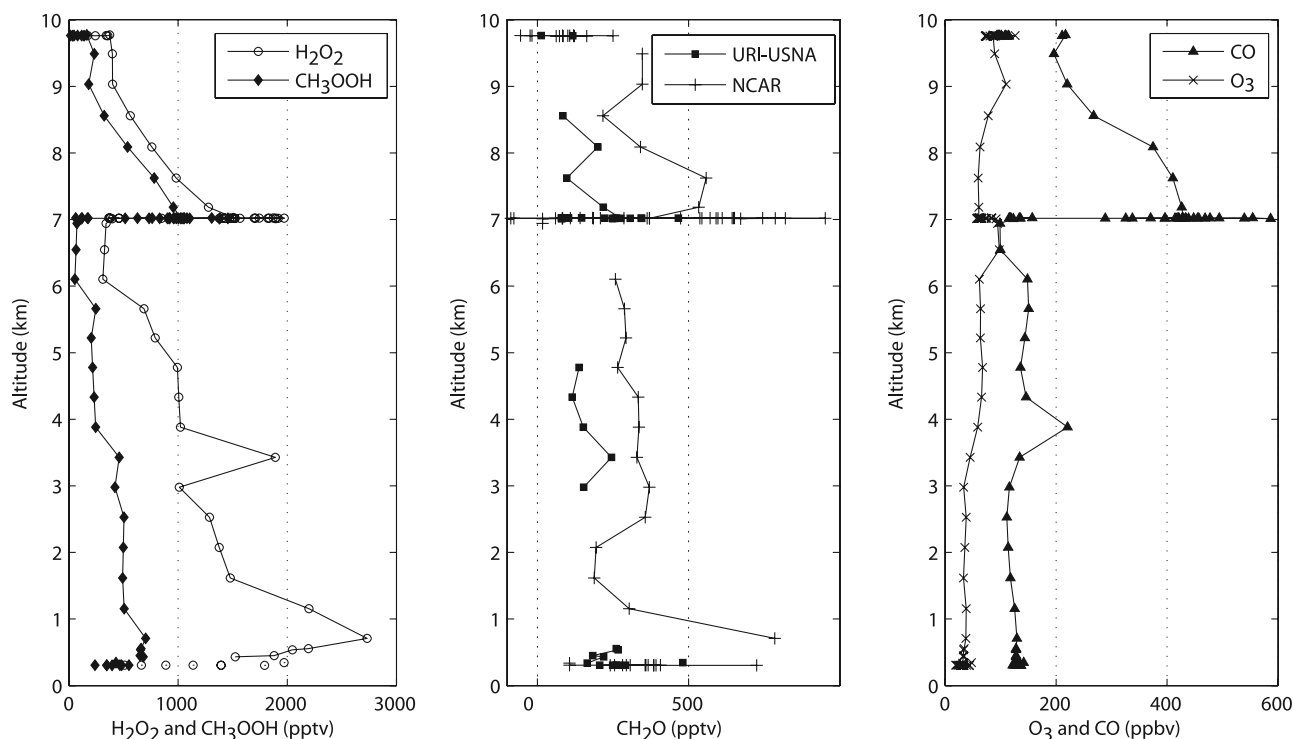


Figure 11. Vertical profiles of H₂O₂, CH₃OOH, CH₂O, O₃, and CO for flight 9. Elevated H₂O₂, CH₃OOH, CH₂O, and CO above 7 km is due to the long-range transport of pollution from biomass burning in Alaska.

[33] The convectively lofted air mass sampled on flight 18 is shown above 6 km in Figure 8. At 6 km, H₂O₂ dropped from ~1000 pptv to ~500 pptv while CH₃OOH increased from ~500 pptv to ~1000 pptv shifting the H₂O₂/CH₃OOH ratio from 2 to 0.5. This is a strong indication that the sampled air was influenced by fresh convection. The use of the H₂O₂/CH₃OOH ratio to identify the convective outflow on flight 18 agrees well with *Bertram et al.* [2006]. These authors use an increase in the NO_x/HNO₃ ratio away from steady state as a tool for identifying fresh convection. *Bertram et al.* [2006] further note that increases in SO₂ (up to 700 pptv) are indicative of recent convective lofting of BL air and point to another possible removal mechanism for H₂O₂ during this event. Elevated short-lifetime species such as ethene (~1.4 days) [*Warneck*, 2000] also support the conclusion that recent convective outflow was sampled along this portion of flight 18. In the outflow, CH₂O levels increased to 750 pptv, values similar to samples collected at 3 km. Since this outflow was older than ~2 hours, these enhancements most likely reflect the vertical transport of reactive hydrocarbons followed by the photochemical production of CH₂O. O₃ also showed a slight enhancement of ~25 ppbv while CO showed a marked step increase at 6 km from 100 ppbv to 140 ppbv. Like flight 7, flight 18 shows clear evidence of UT enhancements of CH₃OOH, CH₂O, O₃, and CO associated with convective outflow.

3.4. Evidence of Biomass Burning: A Case Study of INTEX-NA Flight 9

[34] Flight 9 left Bangor, ME crossing over New Brunswick and the western North Atlantic (Figure 9). A biomass burning plume was sampled during the northern most leg of

this flight. Meteorological conditions during and prior to flight 9 (18 July) consisted of strong westerly flow north of the U.S.-Canada border. Figure 10 shows air mass back trajectories for the biomass-burning plume sampled on 18 July. The trajectories indicated consistent westerly flow up to 5 days prior to sampling and suggest the sampled air mass originated over Alaska between 4 and 5 days prior to 18 July.

[35] An altitude profile of H₂O₂, CH₃OOH, CH₂O, O₃, and CO is shown in Figure 11. At 7 km, the aircraft clearly went through a thin layer of highly polluted air that was mixed up to ~9 km. H₂O₂ and CH₃OOH increased by 1.4 ppbv, reaching 2 and 1.5 ppbv respectively, and remained elevated until 9 km. CH₂O (NCAR) reached 1 ppbv while CO reached 600 ppbv. O₃ mixing ratios peaked only slightly at 7 km and decreased just above the pollution layer. In addition, CO₂, CH₄, and NO, all typical fire emissions [*Yokelson et al.*, 1996, 1997, 1999] were elevated in this plume. These results agree well with observations of other biomass burning plumes around the world [*Lee et al.*, 1997, 1998; *Yokelson et al.*, 1999]. *Lee et al.* [1998] found enhanced H₂O₂, organic hydroperoxides, and CH₂O within biomass burning plumes over the South Atlantic, Brazil, and southern Africa. Direct production within the fires and post photochemical production in the atmosphere produced H₂O₂ and CH₃OOH mixing ratios of up to 14 and 5 ppbv respectively. Unlike the biomass burning plume sampled on INTEX-NA, these samples were collected within the fires, not 4–5 days downwind of the fire, explaining the elevated observations.

[36] H₂O₂, CH₃OOH, and CH₂O increased with CO similar to fire samples measured by *Lee et al.* [1997]. The

INTEX-NA ratio of H₂O₂, CH₃OOH, and CH₂O with respect to CO were 4×10^{-3} , 2×10^{-3} , and 1×10^{-3} compared to Lee *et al.*'s [1997] ratios of $1\text{--}5 \times 10^{-2}$, $2\text{--}4 \times 10^{-3}$, and $7\text{--}19 \times 10^{-3}$. The H₂O₂ and CH₂O ratios were higher because of the age of the INTEX-NA fire plume; photochemical production of H₂O₂ and CH₂O by precursors would increase the ratio over time. The detection of enhanced peroxides and CH₂O in the Alaskan biomass burning plume over the eastern United States indicate an additional source of HO_x precursors to the UT.

4. Conclusions

[37] A comparison of H₂O₂, CH₃OOH, and CH₂O over North America and the North Atlantic during the INTEX-NA, TOPSE, and SONEX aircraft campaigns showed highly variable mixing ratios. Peroxides and CH₂O mixing ratios and variability were larger during INTEX-NA compared to TOPSE and SONEX. Mean H₂O₂, CH₃OOH, and CH₂O were 1390, 440, and 480 pptv respectively, more than two times higher than TOPSE measurements and an order of magnitude higher than SONEX measurements. This is attributed to higher solar radiation levels and the more polluted conditions of INTEX-NA. H₂O₂, CH₃OOH, and CH₂O mixing ratios and variability decreased with altitude for all three gases and on all three campaigns, except for CH₃OOH during TOPSE. In addition, the impact of convection on H₂O₂, CH₃OOH, and CH₂O mixing ratios was investigated. Using the H₂O₂/CH₃OOH ratio, convectively influenced air parcels were found to be enhanced in CH₃OOH, CH₂O, CO, NO, and NO₂ while H₂O₂ and HNO₃ were depleted by wet removal. Given that the lifetime of CH₂O during the summer is ~ 2 hours, the enhanced UT CH₂O in convective case studies represents the transport of and photochemical production by reactive hydrocarbons. In addition to convection, biomass burning was shown to enhance upper troposphere peroxides and CH₂O up to 1.5, 2, and 1 ppbv, respectively. Results from this study suggest the variability of the H₂O₂, CH₃OOH, and CH₂O in the UT is driven by the transport of convectively lofted air masses and nonregional sources in addition to local photochemistry. This implies transport mechanisms are important factors to include in photochemical models simulating upper troposphere H₂O₂, CH₃OOH, and CH₂O.

[38] **Acknowledgments.** The authors would like to thank H. Singh, D. Jacob, J. Crawford, and W. Brune, the pilots and crew of the NASA DC-8, and the INTEX Management group for successfully guiding us through the INTEX-NA campaign. We would also like to thank NASA for supporting this research through grant NNG04GB38G. Additionally, the authors thank G. Sachse, M. Avery, R. Talbot, J. Dibb, E. Scheuer, H. Fuelberg, and D. Westberg for providing additional data and images and J. Merrill for his thoughtful comments and review of this manuscript.

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